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A dynamic liquid support system for continuous electrospun yarn fabrication

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Abstract

Electrospinning is known to be a highly versatile process which is able to produce fibers made out of different compositions with diameter of a few microns down to several nanometers. Current electrospinning technology generally involves the deposition of fibers onto a solid substrate although in some cases, a liquid coagulation bath is used to collect the fibers. However, a liquid collector may offer several advantages over a solid substrate. A novel electrospun fiber manipulation process through the use of a water vortex is described in this communication where continuous yarn was made from electrospun fibers. Preliminary studies on some parameters such as solution feed rate and solution concentration and their impact on fabrication of the yarn and the fiber morphology were carried out.

Keywords: Yarn; Electrospinning; Liquid collector

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1. Introduction

Electrospinning is known to be a simple and versatile method to produce non-woven two-dimensional nanofibrous mesh. The materials that have been electrospun include various polymers and their mixtures, ceramic precursors [2,8,15] and composites [5,24,25]. Electrospinning of ceramic precursors, with or without the addition of polymers has been widely used to fabricate ceramic nanofibers after sintering. Recently, copper nanofiber has been fabricated through appropriate heat-treatment of electrospun copper nitrate and polyvinylbutyral mixtures [1]. The ability to electrospin fibers from such diverse classes of material has resulted in a huge range of potential applications and growing interest in the process by researchers worldwide. Thus, much progress has been made in the understanding and the controlling of the electrospinning process [12]. Currently, various ordered structures such as aligned nanofibers, arrayed nanofibers and controlled deposition of the electrospun fibers have been achieved using different mechanical collection devices and the manipulation of the electric field [22].

In a typical electrospinning set-up, a reservoir is used to contain a solution of sufficient viscosity. The solution is transferred from the reservoir to a spinneret which is generally a blunt tip syringe needle. A pendent drop of solution is allowed to form at the spinneret tip. A high voltage supply is then applied to the solution such that at a critical voltage (about 10 kV) – the electrostatic repulsive force within the solution will cause a fine jet of solution to erupt from the tip of the pendent drop. A collector placed at a distance away will generate a potential difference to that of the charged solution at the tip of the spinneret. It is this potential difference that will cause the charged solution to accelerate towards the collector. The distance between the collector and spinneret will depend on the duration for the solvent to evaporate from the

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solution which is usually from 10 cm to 20 cm. Although the initial portion of the electrospinning jet is stable, it soon enters the bending instability region where there are further stretching and evaporation of the jet causing a non-woven mesh to deposit on a smooth and flat collector [13].

With the exception of non-woven fibrous mesh, obtaining other fibrous architectures from electrospinning is still a challenge to many researchers despite various reported success of obtaining different architectures. Generally electrospun submicron and nanofibers are too weak for conventional physical manipulation due to its small size and low mechanical strength. Electrospun fibers collected on a disk rotating at high speed may exhibit necking [27]. For some polymers, the strength of a single nanofiber may be so weak that it breaks under its own weight [9]. The dynamic interaction between the external electric field and the electrostatic charges on the electrospinning jet makes manipulation of the electric field to precisely control the deposition of the fibers almost impossible. Nevertheless it has been shown that it is possible to control the deposition of the electrospun fibers before the electrospinning jet goes into the bending instability stage. However, the length of the fiber is restricted by the size of the polymer solution droplet at the spinneret tip and this negates the high production capability of the process [18]. While most collectors for the electrospun fibers are in the form of a solid substrate, some researchers have used liquid media as a collector. In most cases, the liquid media is mainly used as a coagulation bath [17,7]. However, Smit et al. has demonstrated that continuous yarn made from electrospun fibers can be collected off the surface of a static liquid media [16].

We hypothesized that a dynamic liquid substrate can be used as a unique platform and tool for the manipulation of nanofibers. Liquid properties such as surface tension, viscosity, interfaces and hydrodynamic interactions, can be used to control the electrospun fibers. Unlike a rigid solid substrate, a micro-component on a liquid substrate can be easily maneuvered and this advantage has been adopted in the self-assembly of micro-structures [19]. Fluid interfaces and hydrodynamic interaction have also been used for the assembly of particles [4]. In this paper, we have demonstrated that a liquid system may have the potential to address the limitations of the current state-of-the-art such as manipulation of the electrospun fibers without breaking them, and forming various assemblies. We used a vortex created from water flowing out from the bottom of a basin as a dynamic liquid system to fabricate continuous yarn. The continuous yarn can be collected at a speed of over 60 m/min. Preliminary studies on parameters such as solution concentration and solution feed rate on the yarn fabrication process were investigated and discussed.

2. Experimental

Poly(vinylidene flouride-*co*-hexafluoropropylene) (PVDF-*co*-HFP) (Aldrich, Mw 455,000) was dissolved in a mixture of 40% dimethylacetamide and 60% acetone, heated to 60 °C, to give a concentration of 0.12 g/ml. To investigate the effect of solution concentration on fiber diameter, two other concentrations of 0.08 g/ml and 0.1 g/ml were prepared. All chemicals were used as received without further modification.

Fig. 1 shows the experimental set-up used to generate electrospun yarn. A vortex was formed on the basin through a hole of diameter 5 mm created at its base as the water drains out into a tank placed below. A pump was used to recirculate the water from the tank back to the basin and the water level in the basin was maintained at a constant height. A wire was

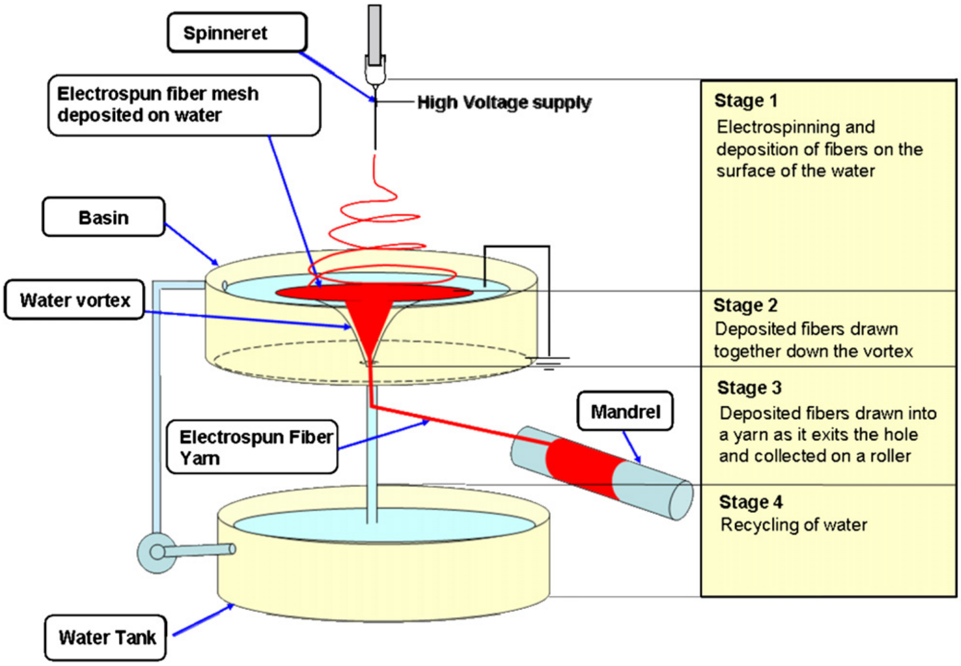

Fig. 1. Schematic of the steps for the formation of yarn using a vortex.

inserted into the basin to remove any residual charges on the water surface. A rotating mandrel was used to collect the resultant yarn emerging from the bottom of the basin.

Electrospinning was carried out by connecting a high voltage power supply from Gamma High Voltage Research HV. A voltage of 12 kV was applied to the spinneret with the distance from the tip of the spinneret to the surface of the water maintained at 12 cm. The spinneret used was a B-D 27G1/2 needle which was ground to give a flat tip. A KD Scientific syringe pump was used to provide a constant feed rate. To study the effect of feed rate on yarn formation, the feed rate was varied from 1 ml/h, 2 ml/h, 5 ml/h, 10 ml/h to 15 ml/h for a concentration of 0.12 g/ml polymer solution. For all other polymer concentrations the feed rate was maintained at 10 ml/h.

The yarn, which was carried by the falling water from the top basin, was manually transferred to the rotating mandrel to initiate take-up. The speed of the rotating mandrel was adjusted such that the yarn from the falling water was collected. A scanning electron microscope (SEM), Quanta FEG 200, FEI, Netherlands, was used to view the yarn microstructure. Samples were first coated with gold using a JEOL JFC-1600 Auto Fine Coater before viewing under SEM. The diameter of the fibers in the yarn was determined by the SEM images.

3. Results and discussions

The electrospinning process leading to the deposition of fiber on a collector for both a solid substrate and a liquid substrate follows the same principle. Since the fiber collected on a solid substrate is continuous, so is the fiber collected on a liquid substrate, provided there is no disruption to the electrospinning process. In general, parameters affecting the formation and morphology of the fiber deposited on a solid substrate [12] also apply to the fiber deposited on a liquid substrate. The main difference between the two collecting systems is the ability to manipulate the deposited fiber mesh to form desirable fibrous architectures. While modifying the fibrous architecture deposited on a solid substrate without damaging the fiber is near impossible, on a liquid substrate, the deposited fibers can be easily rearranged to form other assemblies.

In the following sections, we will discuss the different parameters that affect the physical characteristics of the fiber and the yarn. Generally, the fibers that make up the yarn are directly affected by the electrospinning condition. However, the yarn characteristic and its production are affected by its constituent fiber morphology and the deposition area and location of the fiber on the basin.

3.1. Fiber formation

Since the yarn is made out of fibers, any effect on the characteristic of the fiber will have an impact on the resultant yarn. Yarn made out of fiber with sub-micron diameter will have a higher surface area compared to another that is made out of fiber with larger diameter. The parameters that affect the fiber morphology are generally similar to those found in normal electrospinning process where a solid plate collector is used. One of the main parameters that affect the fiber diameter is the concentration of the solution to be electrospun. By varying the concentration of the solution, beaded or smooth fiber can be obtained. The fiber diameter may also be affected by the feed rate of the solution.

3.1.1. Concentration effect on individual fiber

In electrospinning, many researchers have shown that by reducing the concentration of the polymer solution, fibers of smaller diameter can be obtained [20,11]. In agreement with their results, there was a decrease in fiber diameter with lower polymer concentration as given in Table 1. However, beaded fibers were obtained at the lowest concentration of 0.08 g/ml (Fig. 2). At a higher concentration of 0.1 g/ml, fewer beads were observed on the fiber while completely smooth fibers were obtained when the solution concentration was increased to 0.12 g/ml. The polymer concentration will affect the ability to form continuous yarn and this will be covered in Section 3.2.1.

Detailed studies on the various parameters that influence bead formation have been covered by various researchers and will not be discussed here [3,14,26]. Briefly, a higher surface tension will favor the formation of beads since surface tension reduces surface area per unit mass by changing the jet to spherical. To reduce the formation of beads, a solution of higher viscosity which allows the solution to be stretched and minimize the effect of surface tension, is preferred.

3.1.2. Feed rate effect individual fiber

It can be seen from Table 2 that with increased feed rate, there was a corresponding increase in the diameter of the individual fibers. With a higher feed rate, more solution was drawn from the tip of the spinneret. While maintaining the same voltage and distance from the spinneret tip to the water, the increased volume of solution would result in an increase in the fiber diameter. It was also observed that as the feed rate increased, the variation in fiber diameter also increased as shown in Table 2. This could be due to the difference in the coagulation rate of fibers in contact with the water upon deposition. As PVDF-*co*-HFP is hydrophobic, it is highly probable that not all the deposited fibers will be in complete contact with the water upon deposition. The fibers in contact with water will instantaneously 'precipitate' out, as water is a non-solvent for the polymer. Subsequent lengths of the fibers may deposit on these previous fiber segments and solidify at a slower rate with a greater reduction in diameter. It has been also reported by Theron et al. [23] that an increased feed rate will result in a smaller deposition area. As the feed rate increases, this

Table 1
Concentration of polymer solution versus average fiber diameter at a feed rate of 10 ml/h

Concentration (g/ml)	Average fiber diameter (nm)	Standard deviation (nm)
0.08	463	157
0.1	723	226
0.12	1224	393

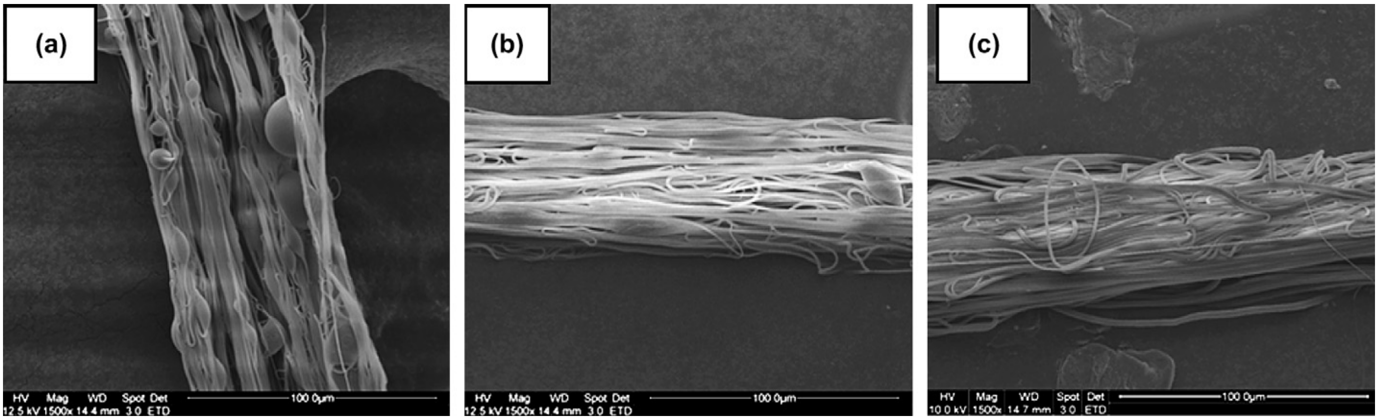

Fig. 2. Physical appearance of yarns at different electrospinning concentrations: (a) beaded fibers at concentration of 0.08 g/ml; (b) less beaded fibers at concentration of 0.1 g/ml; (c) smooth fibers at concentration of 1.2 g/ml.

Table 2
Fiber diameter with respect to feed rate

Feed rate (ml/h)	Average fiber diameter (nm)	Standard deviation (nm)
1	740	150
2	770	154
5	1190	288
10	1220	393
15	1300	429

difference in solidification rates will intensify as more mass is generated per unit time and area and thus a larger variance in diameter was observed.

From Table 2, it can be seen that between a feed rate of 2 ml/h and 5 ml/h, there was a significant increase in the fiber diameter. Studies have shown that an electrospinning jet may undergo secondary bending instabilities due to its high charge density and would result in smaller fiber diameters [13,10]. As the feed rate of the solution is increased, the charge density will decrease. Thus, it is possible that with a lower feed rate of 2 ml/h or less, the electrospinning jet undergoes secondary bending instability. However, at a higher feed rate of 5 ml/h or more, this may not occur. Although the electrostatic repulsion within the solution may be sufficient to initiate the electrospinning process despite the larger initial volume, the electrostatic forces may not be strong enough to create more bending in the thicker electrospinning jet.

3.2. Yarn formation

During the electrospinning process, fiber was deposited on the surface of the water. Due to the presence of the vortex, fibers deposited close to the vortex were pulled along with the falling water through the hole at the bottom of the basin and simultaneously bundled together to form a continuous yarn. The yarn was manually transferred onto a rotating mandrel to initiate the yarn take-up after which the process became continuous. Continuous deposition of fibers from the electrospinning above will feed the yarn drawing process as the moving water continuously carries the deposited fibers through the hole at the bottom of the basin, which was then taken up by the rotating mandrel in the form of a yarn. A schematic of the events that lead to the formation of the yarn is shown in Fig. 1.

The resultant yarn wound onto the mandrel was made out of highly aligned fibers. As the deposited fiber flows with the vortex, the fiber mesh elongates and consolidates in the direction of the flow of the water. Fig. 3 shows the comparison of a PVDF-*co*-HFP yarn that was collected in the tank without going through the drawing process and one that was collected on the mandrel. Without going through the drawing process

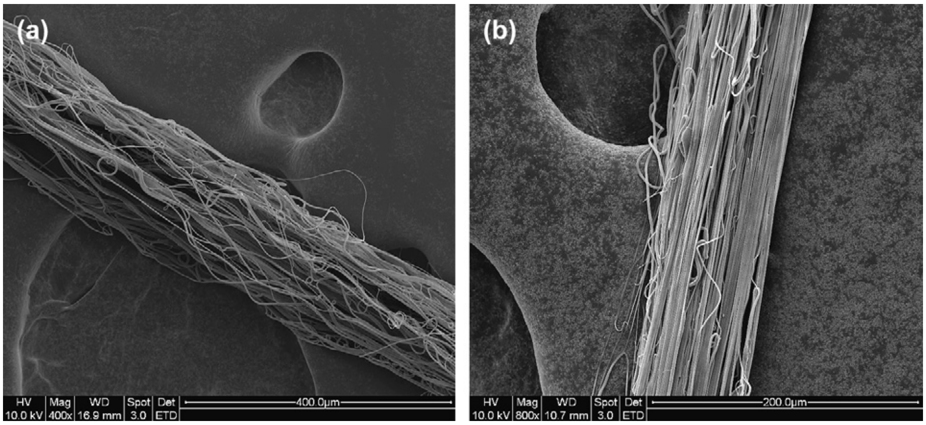

Fig. 3. SEM images of the collected yarn: (a) without going through the drawing process in the air; (b) after going through the drawing process in the air.

onto the rotating mandrel, the fibers in the yarn were 'wavy' although it is generally aligned in the long axis. However, after the yarn was drawn onto the mandrel, the fibers in the yarn were 'straightened' and highly aligned in the direction of the long axis. This is probably due to the drawing process which exerts a tension on the yarn that straightens the fibers. Moreover, the presence of water in the yarn may act as a lubricant that allows slipping of the individual fibers without breaking them and its surface tension will further compress the yarn into a tight bundle. 'Kinks' were observed on the yarn as a result of the elongation and consolidation of the deposited nonwoven mesh as it passes through the hole. Smit et al. suggested that the surface tension of water assisted in the pulling and aligning of the fiber into a circular diameter yarn structure [16]. In an earlier study, we had demonstrated that surface tension of water can be used to bring stray, individual electrospun fibers together to form a tight bundle [21].

3.2.1. Effect of concentration on yarn formation

Decreasing the concentration of the solution has been found to reduce the diameter of the individual fiber and resulted in the formation of beaded fibers. A lower concentration of the solution was also found to have an impact on the ability to form continuous yarn. At the feed rate of 10 ml/h, yarn formed from solution concentration of 0.08 g/ml was not continuous while continuous yarn can be fabricated when concentrations of 0.1 g/ml and 0.12 g/ml were used. With a lower concentration, there was greater number of beads found in the fiber and studies have shown that the presence of beads would reduce the mechanical strength of electrospun fiber. This could be due to reduced cohesive force between the fibers [6] for beaded fibers. Thus the strength of the yarn may be too weak to withstand the drawing process and results in yarn breakage.

3.2.2. Effect of feed rate on yarn formation

It was observed that the feed rate of polymer solution had a significant effect on the yarn spinning process. For solution feed rate of 1 ml/h and 2 ml/h, the yarn take-up speed was 58 m/min. However, for higher feed rate of 5 ml/h, 10 ml/h and 15 ml/h, the take-up speed was 63 m/min. The take-up speed was set as the minimum speed at which the yarn can be drawn onto the rotating mandrel without it being washed into the tank below. At a higher feed rate, it was necessary to increase the take-up speed of the yarn to 63 m/min to prevent it from being washed into the tank and enable continuous drawing of the yarn. Since the volumetric flow of water is constant, the factor that led to the increase in the take-up speed could be due to surface tension or it could be the result of the higher mass of the yarn spun at higher feed rate. However, more tests would need to be carried out to determine the dominant parameter that affects the take-up speed of the yarn.

For the continuous drawing of yarn, a feed rate of more than 5 ml/h is preferred. At a feed rate of less than 5 ml/h, there is a tendency for the yarn to "break". This can be understood from the fact that as a single strand, fiber with diameter in the sub-micron and nanometer level is weak. Similarly, the yarn must be collected in a bundle with sufficient ultrafine fibers such that the mechanical strength of the bundle is able to withstand the drawing and winding process. The accumulation of the fibers through the electrospinning process must be much faster than the flowing water through the hole. In this case a higher polymer solution feed rate is preferred to ensure sufficient accumulation of deposited fibers on the surface of the water to be drawn into a yarn. Thus, subsequent experiments to study the effect of feed rate on yarn morphology were carried out using feed rates of 5 ml/h, 10 ml/h and 15 ml/h and a constant take-up speed of 63 m/min.

As seen from Fig. 4 the average yarn diameter increased linearly with the feed rate. However, the scatter in the yarn diameter also increases with increasing feed rate. Given the same flow rate of the water through the hole at the bottom of the collection basin, the speed at which the deposited fibers were brought together down the vortex to form the yarn was relatively unchanged. Assuming that no fibers were lost in the process, conservation of mass will mean that the increase in the feed rate will bring about a corresponding increase in the yarn diameter. The increase in the scatter of the yarn diameter with feed rate could be due to a few factors. As seen from Table 2, with higher feed rate, the standard deviation for the single electrospun fibers that make up the yarn also increases. This will naturally contribute to an increase in the scatter of the resultant yarn diameter. The speed of the flowing water around the vortex and the location of deposition of the fiber play a significant role in the large scatter of the resultant yarn diameter. At the edge of the vortex, water spirals quickly down the vortex into the hole. However, at a slight distance away from the vortex edge, the flow of the water is in a circumferential manner around the vortex instead of flowing directly into it. Thus as the fibers were randomly deposited around the edge of the vortex, the amount of fibers that was drawn down the vortex became inconsistent. This impact is even more apparent for a higher feed rate where a greater mass of fiber was deposited at any given time. As a result, with greater feed rate, the variation in the yarn diameter would also increase. Another reason for the higher distribution of yarn diameter with feed rate is the deposition area of the fiber on the water surface. For small feed rates, the fiber diameter will be small and there will be a greater spread in the fiber deposition which will

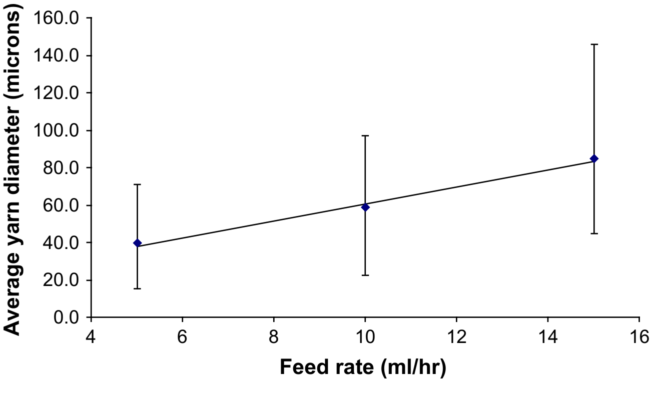

Fig. 4. Graph of average yarn diameter against feed rate. The vertical line for each point depicts the scatter in the yarn diameter for each feed rate.

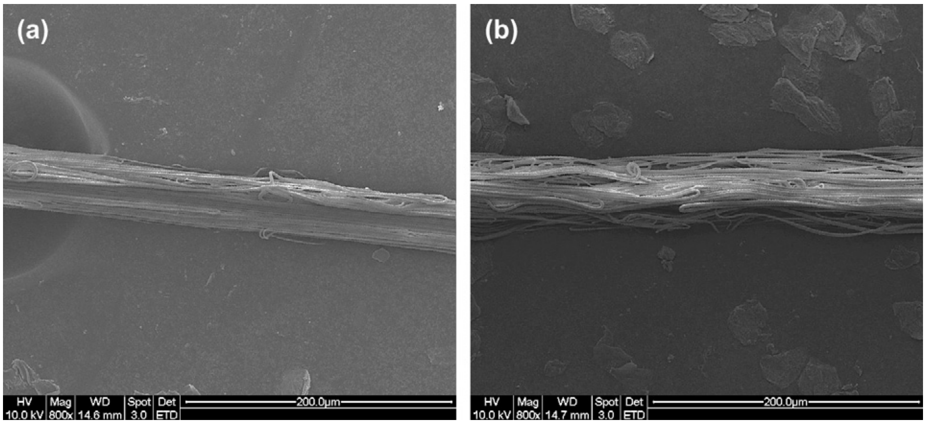

Fig. 5. Fiber entanglement in the yarn: (a) yarn obtained from drawing of fiber spun at feed rate of 5 ml/h showing less fiber entanglements; (b) yarn obtained from drawing of fiber spun at feed rate of 10 ml/h showing greater fiber entanglements.

result in a less entangled fiber mesh. Thus as the yarn was drawn onto a rotating mandrel, the fiber in a less entangled mesh will elongate and align to form a more compact and uniform yarn due to the tension applied. The deposition area of the fiber depends on the charge density on the surface of the electrospinning jet. A higher feed rate will have a lower charge density [23] and the fiber will be deposited over a smaller area. Coupled with the faster fiber deposition, it results in a far greater entanglement in the fiber mesh as compared to a smaller feed rate. This greater amount of fiber entanglement will offer greater resistance to fiber alignment when there is a tension applied through the drawing process onto the rotating mandrel as shown in Fig. 5. Finally, the large variation in yarn diameter could be attributed to the constant take-up speed used for the different feed rates studied. Although a constant speed was set, it may not be optimal for each feed rate used in this experiment. The optimization of take-up speed for different feed rates is currently under investigation. As a result of the above-mentioned factors, the scatter in the yarn diameter was found to increase with feed rate.

4. Conclusion

In this paper, we described a new system of assembling the electrospun fiber mesh using water as the supporting and working media to manipulate the deposited electrospun fibers into a continuous yarn. The vortex created aided in the yarn formation and facilitated yarn collection. The effect of the two parameters, feed rate and polymer concentration on the yarn morphology, was studied. Although yarn of varying diameters can be achieved by varying the feed rate, there is a minimum feed rate required for continuous yarn to form without any breakage. However, at a higher feed rate, the fiber diameter is more than 1 μm and the deviation in the yarn diameter is large. To maintain the higher feed rate, it is still possible to fabricate yarn from fibers in the sub-micron level by reducing the polymer concentration. However, it is noteworthy that reduction in concentration below a threshold also affects the production of continuous yarn. Besides these, there are other parameters such as take-up speed, velocity of the water in the vortex, nature of the polymer, applied voltage, etc., which also affect the yarn formation and characteristics. Further studies are being carried to examine how other electrospun fiber structure can be constructed through the control of liquid flow and its properties.

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